

Supplementary material for the article:

Malenov, D. P.; Zarić, S. D. Chelated Metal Ions Modulate the Strength and Geometry of Stacking Interactions: Energies and Potential Energy Surfaces for Chelate-Chelate Stacking. *Physical Chemistry Chemical Physics* **2018**, 20 (20), 14053–14060.
<https://doi.org/10.1039/c7cp06262a>

SUPPORTING INFORMATION

CCSD(T)/CBS interaction energies for the selected chelate-chelate stacking geometries

Due to its excellent performance in calculating the stacking of nickel chelate with benzene, the M06HF functional with Grimme D3 dispersion correction and with def2-TZVP basis set was used in order to find the optimal normal distances for the geometries chosen for CCSD(T)/CBS calculations of interaction energies (Figure S1). The CCSD(T)/CBS interaction energies were then obtained for these geometries using the method of Mackie and DiLabio and by taking into account the same basis set dependence of MP2 and CCSD(T).

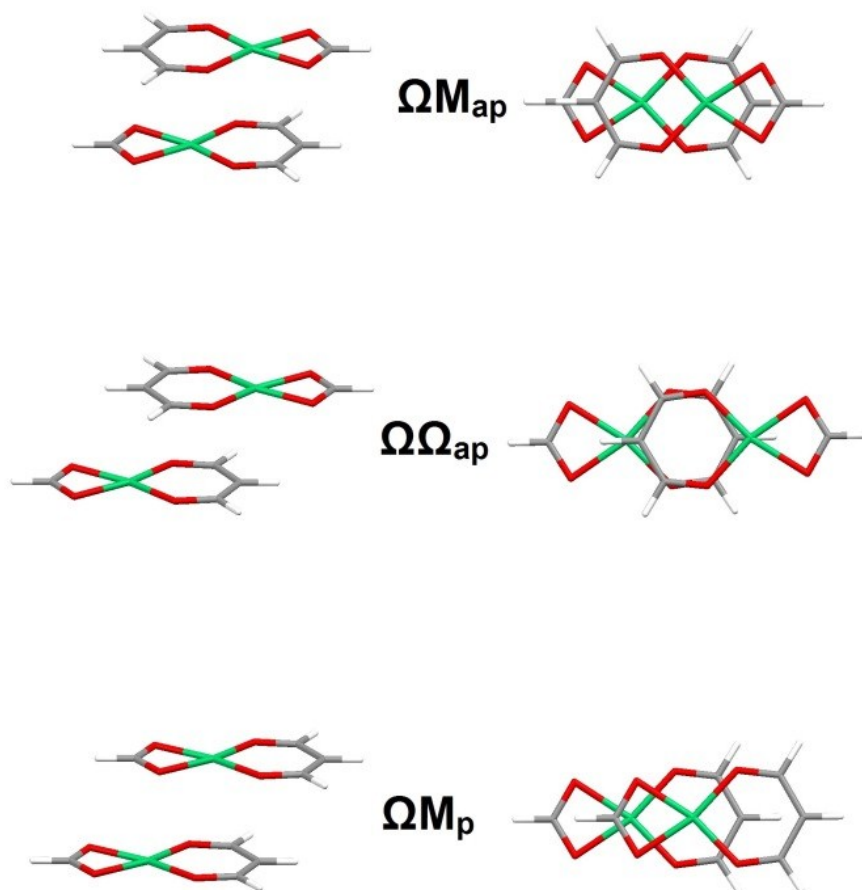


Figure S1. Selected geometries for which CCSD(T)/CBS stacking energies were calculated. In ΩM_{ap} the chelates in antiparallel orientation, with center of one chelate above the metal of the other chelate, and vice versa. In $\Omega\Omega_{ap}$ the chelates are in antiparallel orientation, with center of one chelate above the center of the other chelate. In ΩM_p the chelates are in parallel orientation, with center of one chelate above the metal of the other chelate, and vice versa.

Table S1. Interaction energies of CCSD(T)/CBS geometries for chelate-chelate stacking (Figure S1), calculated at CCSD(T)/CBS level and at various DFT levels

GEOMETRY		ΔE [kcal/mol]				
		CCSD(T)/CBS	M06HF-D3/ def2-TZVP	ω B97XD/ def2-TZVP	B3LYP-D3/ aug-cc-pVDZ	LC- ω PBE-D3BJ/ aug-cc-pVDZ
Ni	ΩM_{ap}	-7.35	-7.59	-6.88	-7.15	-7.62
	$\Omega\Omega_{ap}$	-8.32	-10.69	-7.37	-7.61	-8.49
	ΩM_p	-4.56	-3.86	-4.28	-4.40	-4.58
Pd	ΩM_{ap}	-8.63	-7.86	-8.36	-9.41	-8.95
	$\Omega\Omega_{ap}$	-8.17	-8.84	-7.88	-7.79	-8.52
	ΩM_p	-5.77	-4.21	-6.00	-7.08	-5.95
Pt	ΩM_{ap}	-8.79	-7.39	-9.50	-11.97	-8.79
	$\Omega\Omega_{ap}$	-7.57	-6.91	-9.40	-9.87	-7.90
	ΩM_p	-6.28	-4.09	-7.96	-9.26	-6.17

Potential energy curves for additional model systems

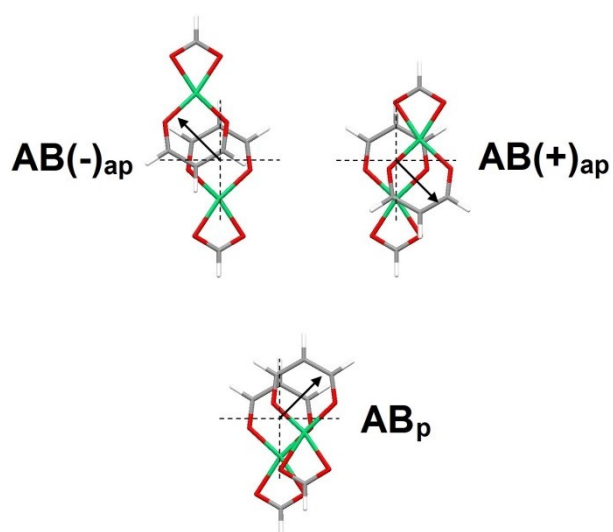


Figure S2. Additional model systems for the study chelate-chelate stacking, the chelates were displaced along the line forming 45° angle with the C₂ axis of the *acac* type chelate. For antiparallel orientation (AB_{ap}) negative (metals depart from one another) and positive direction (metals approach one another) is possible.

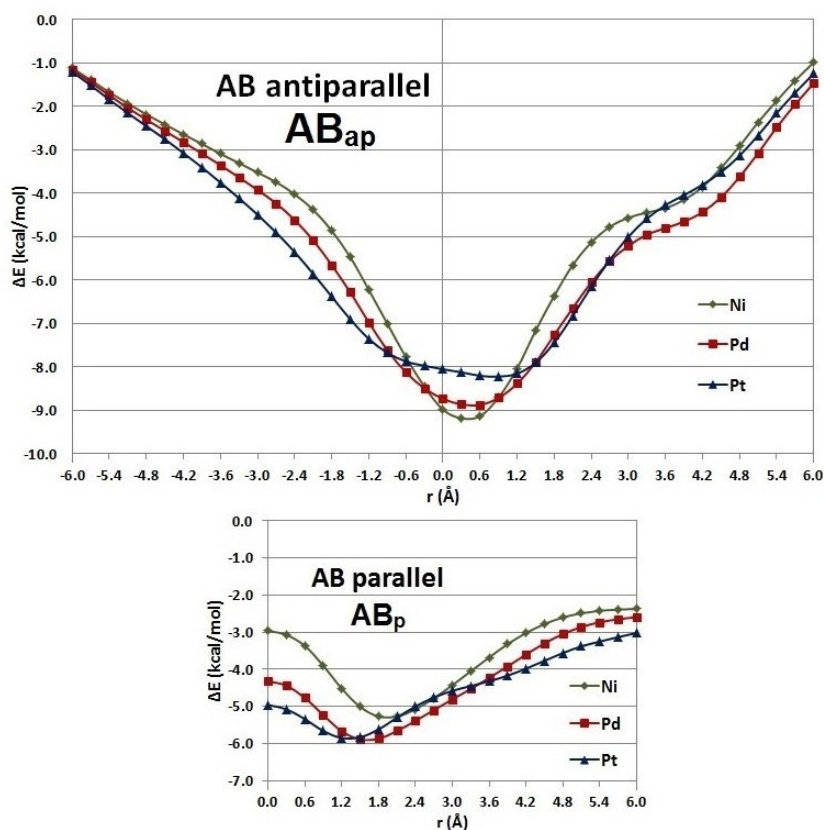


Figure S3. Potential energy curves for AB model systems calculated at LC-ωPBE-D3BJ/aug-cc-pVDZ level of theory.

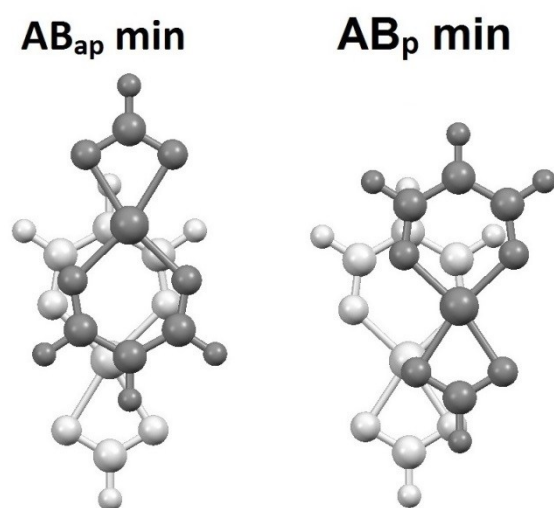


Figure S4. Geometries of minima on potential energy curves for AB model systems

Table S2. LC- ω PBE-D3BJ/aug-cc-pVDZ interaction energies for minima on AB potential energy curves

ANTIPARALLEL	offset [Å]			LC- ω PBE-D3BJ/aug-cc-pVDZ INTERACTION ENERGY [kcal/mol]		
	Ni	Pd	Pt	Ni	Pd	Pt
AB _{ap} min	0.3	0.6	0.9	-9.18	-8.87	-8.22
AB _p min	1.8	1.5	1.2	-5.27	-5.89	-5.85

Normal distances for chelate-chelate stacking

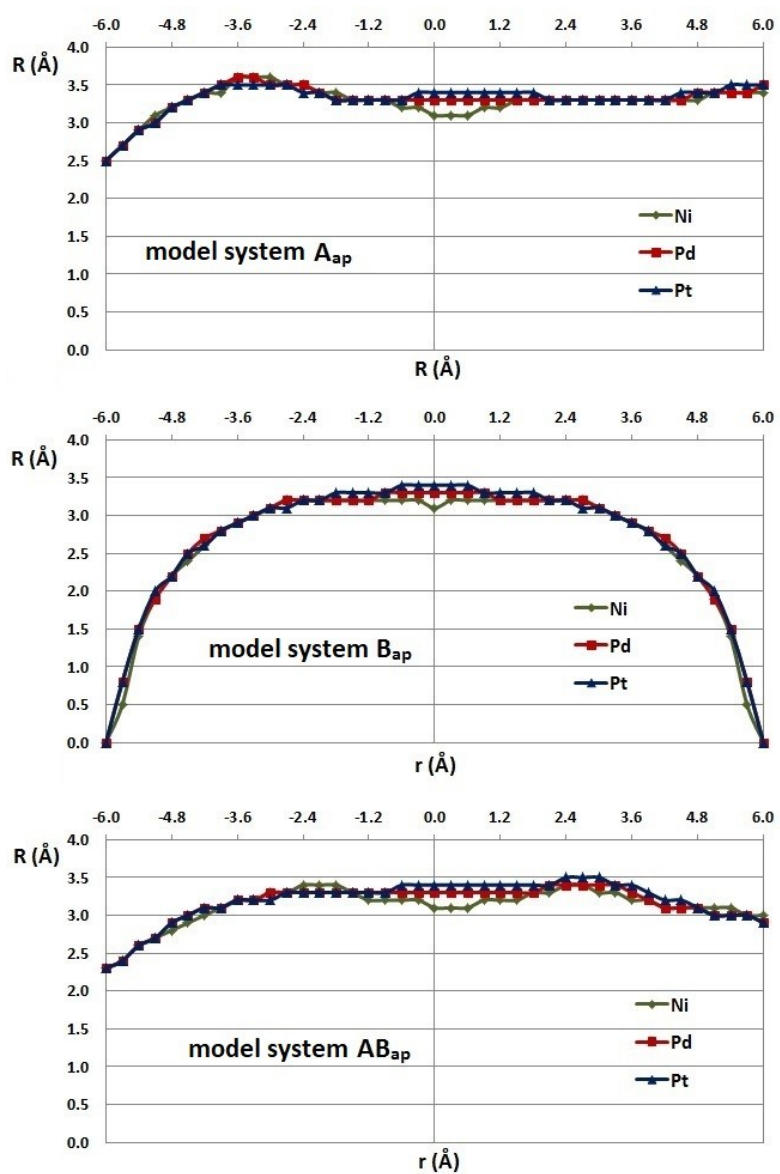


Figure S5. Optimal normal distances for chelate-chelate stacking in antiparallel orientation calculated at LC- ω PBE-D3BJ/aug-cc-pVDZ level of theory

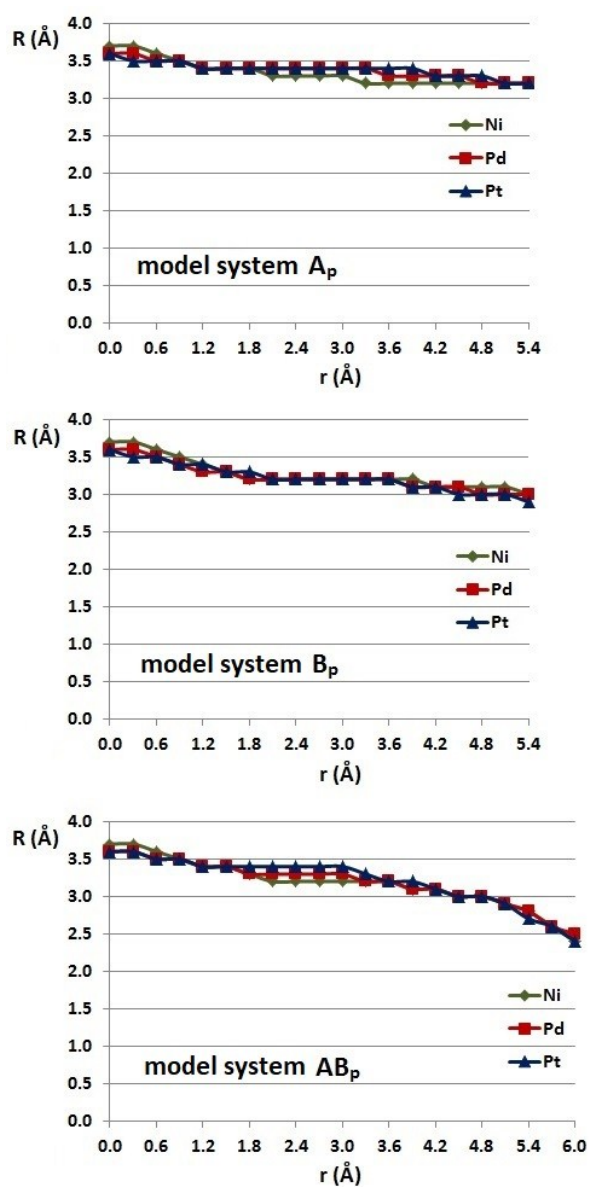


Figure S6. Optimal normal distances for chelate-chelate stacking in parallel orientation calculated at LC- ω PBE-D3BJ/aug-cc-pVDZ level of theory

Overlapping of electrostatic potentials

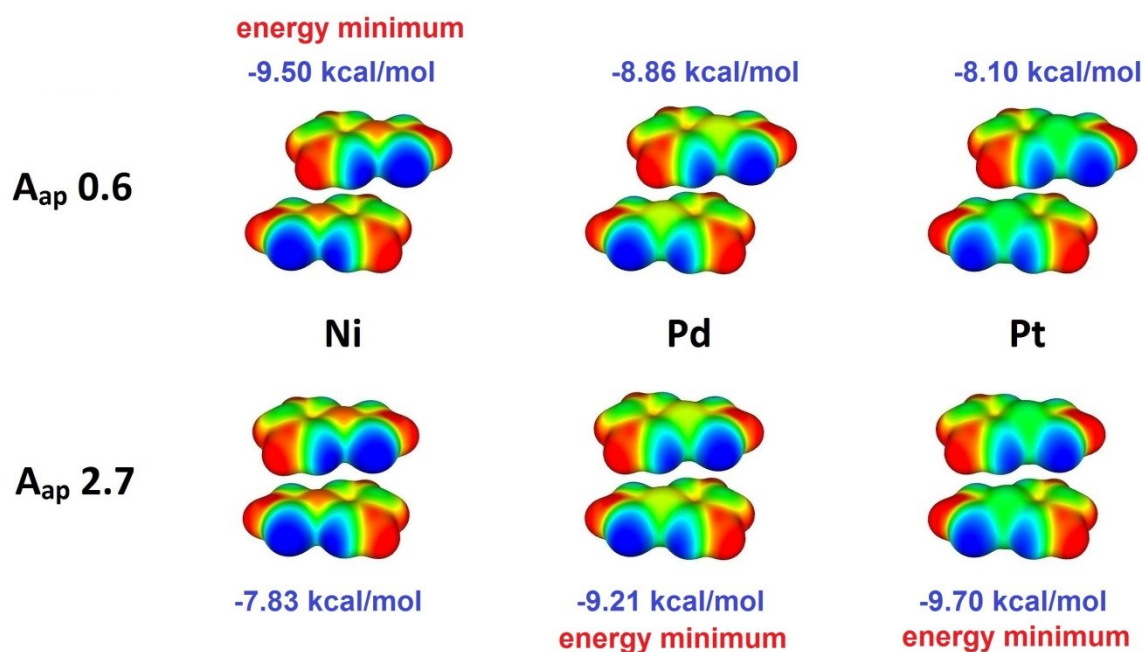


Figure S7. Overlapping of electrostatic potentials of *acac* type chelate rings in antiparallel orientation in two different geometries. The given energies were calculated at CCSD(T)/CBS level of theory.

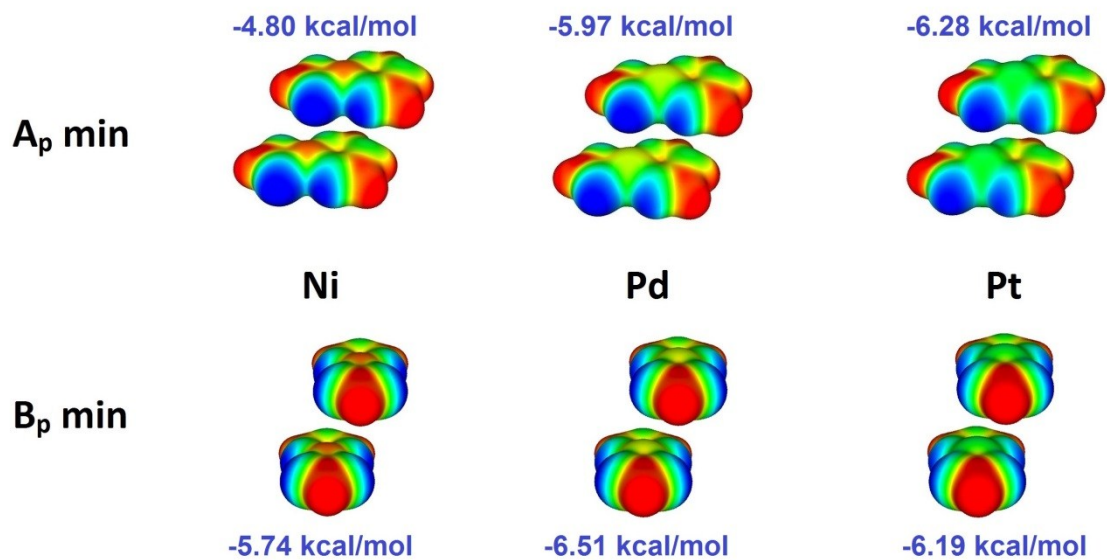


Figure S8. Overlapping of electrostatic potentials of *acac* type chelate rings in parallel orientation in minimum geometries. The given energies were calculated at LC- ω PBE-D3BJ/aug-cc-pVDZ level of theory.